

294-98 PCT/US

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR

09/763380

INTERNATIONAL APPLICATION NO.
PCT/NL99/00568INTERNATIONAL FILING DATE
13 September 1999PRIORITY DATE CLAIMED
11 September 1998TITLE OF INVENTION
Oxidation of Starch

APPLICANT(S) FOR DO/EO/US

Ronald Peter Wilhelmus KESSELMANS and Ido Pieter BLEEKER

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1).
4. A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date.
5. A copy of the International Application as filed (35 U.S.C. 371 (c) (2))
 - a. is transmitted herewith (required only if not transmitted by the International Bureau).
 - b. has been transmitted by the International Bureau.
 - c. is not required, as the application was filed in the United States Receiving Office (RO/US).
6. A translation of the International Application into English (35 U.S.C. 371(c)(2)).
7. A copy of the International Search Report (PCT/ISA/210).
8. Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. are transmitted herewith (required only if not transmitted by the International Bureau).
 - b. have been transmitted by the International Bureau.
 - c. have not been made; however, the time limit for making such amendments has NOT expired.
 - d. have not been made and will not be made.
9. A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
10. An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
11. A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).

Items 13 to 20 below concern document(s) or information included:

13. An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. A **FIRST** preliminary amendment.
16. A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. A substitute specification.
18. A change of power of attorney and/or address letter.
19. Certificate of Mailing by Express Mail
20. Other items or information:

Copy of the PCT application as published under International Publication Number WO 00/15670.

EXPRESS MAIL CERTIFICATE

Date 02/21/01 Label No. EL608284565US
 I hereby certify that on the date indicated above, I
 deposited this paper or fee with the U.S. Postal Service &
 that it was addressed for delivery to the Assistant
 Commissioner for Patents, Washington, D.C. 20231
 by "EXPRESS MAIL Post Office to Addressee" Service.

CASSANDRA LEMS
Name (Print)Cassandra Lems
Signature

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR
09/763380INTERNATIONAL APPLICATION NO.
PCT/NL99/00568ATTORNEY'S DOCKET NUMBER
294-98 PCT/US

21. The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :

| | |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO and International Search Report not prepared by the EPO or JPO | \$1,000.00 |
| <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO | \$860.00 |
| <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO | \$710.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) but all claims did not satisfy provisions of PCT Article 33(1)-(4) | \$690.00 |
| <input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(1)-(4) | \$100.00 |

CALCULATIONS PTO USE ONLY**ENTER APPROPRIATE BASIC FEE AMOUNT =****\$860.00**Surcharge of **\$130.00** for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). 20 30**\$0.00**

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | |
|--------------------------------------------------|--------------|--------------|-------------------------------------|-----------------|
| Total claims | 11 - 20 = | 0 | x \$18.00 | \$0.00 |
| Independent claims | 1 - 3 = | 0 | x \$80.00 | \$0.00 |
| Multiple Dependent Claims (check if applicable). | | | <input checked="" type="checkbox"/> | \$270.00 |

TOTAL OF ABOVE CALCULATIONS = **\$1,130.00**

Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).

\$0.00**SUBTOTAL =** **\$1,130.00**Processing fee of **\$130.00** for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). 20 30

+

\$0.00**TOTAL NATIONAL FEE =** **\$1,130.00**

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).

\$0.00**TOTAL FEES ENCLOSED =** **\$1,130.00**

| | |
|------------------------|----|
| Amount to be: refunded | \$ |
| charged | \$ |

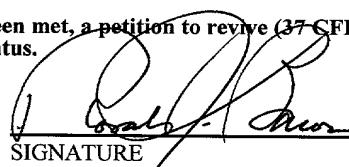
 A check in the amount of **\$1,130.00** to cover the above fees is enclosed. Please charge my Deposit Account No. in the amount of to cover the above fees. A duplicate copy of this sheet is enclosed. The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. **08-2461** A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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SIGNATURE

Ronald J. Baron

NAME

29,281

REGISTRATION NUMBER

21 February 2001

DATE

PATENT



IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Kesselmans, et al.

Serial No: 09/763,380

Filing Date: February 21, 2001

For: OXIDATION OF STARCH

Assistant Commissioner for Patents
Washington, DC 20231

Examiner: Unassigned

Group Art Unit: Unassigned

Docket: 294-98 PCT/US

Dated: March 9, 2001

I hereby certify this correspondence is being deposited with the United States Postal Service as first class mail, postpaid in an envelope, addressed to: Assistant Commissioner for Patents, Washington, D.C.

20231 on March 9, 2001
Dated: 3/9/01, J. Casch

PRELIMINARY AMENDMENT

Sir:

Applicants respectfully submit the following Preliminary Amendment for entry in the above-identified application prior to examination.

IN THE SPECIFICATION:

On page 1, before line 1, please insert the following before the first paragraph:

BACKGROUND OF THE INVENTION

On page 2, line 29, please insert the following:

SUMMARY OF THE INVENTION

On page 3, before line 1, please insert the following before the first paragraph:

DETAILED DESCRIPTION OF THE INVENTION

IN THE CLAIMS:

Please cancel claims 9 and 10 without prejudice.

Please amend claims 3-8 as follows:

3. (Amended) A process according to claim 1, wherein the catalyst is present in an amount ranging from about 5 ppb to about 5000 ppb, preferably from 100 ppb to about 1000 ppb, on dry substance of starch.

4. (Amended) A process according to claim 1, wherein the divalent copper ions are enhanced by one or more of calcium, vanadium, manganese, iron or tungsten ions.

5. (Amended) A process according to claim 1, wherein the starch is a potato starch or tapioca starch.

6. (Amended) A process according to claim 1, wherein the hydrogen peroxide is used in an amount ranging from 0.01 to 5.0 wt%, preferably from 0.05 to 2.5 wt% on dry substance of starch.

7. (Amended) A process according to claim 1, wherein the derivative of the starch is a cationic, anionic or amphoteric starch.

8. (Amended) An oxidized starch obtainable by a process according to claim 1.

Please add new claims 11-18, as follows:

11. A binder in paper coatings or surface coatings comprising an oxidized starch according to claim 1.

12. An adhesive comprising an oxidized starch according to claim 1.

13. A warp yarn sizing comprising an oxidized starch according to claim 1.
14. A coating for glass fibers comprising an oxidized starch according to claim 1.
15. An abrasive paper additive comprising an oxidized starch according to claim 1.
16. A food product additive comprising an oxidized starch according to claim 1.
17. A blanket adhesive comprising an oxidized starch according to claim 1.
18. An emulsifying agent for an alkyl succinic anhydride, alkyl ketene dimer or alkyl isocyanate comprising an oxidized starch according to claim 1.

AFTER THE CLAIMS

Please insert, after the claims, on a separate sheet:

ABSTRACT

The invention relates a process of oxidizing starch wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions. The present invention further relates to an oxidizable starch obtainable by a process comprising treating a starch with

hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

For convenience purposes, a copy of the Abstract is attached hereto on a separate sheet.

REMARKS

Applicants have undertaken to cancel claims 9 and 10, amend claims 3-8, and add new claims 11-18 in the above-identified application in order to remove improper multiple dependencies and conform to U.S. practice. No new matter has been added. In addition, headings and an abstract have been added to the specification. Accordingly, entry hereof and examination on the merits are respectfully requested.

Respectfully submitted,



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ABSTRACT

The invention relates a process of oxidizing starch wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions. The present invention further relates to an oxidizable starch obtainable by a process comprising treating a starch with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

09/763,380 2/21/01 5

VERSION OF AMENDMENT WITH MARKINGS
TO SHOW CHANGES MADE

IN THE SPECIFICATION

On page 1, before line 1, please insert the following before the first paragraph:

BACKGROUND OF THE INVENTION

On page 2, line 29, please insert the following:

SUMMARY OF THE INVENTION

On page 3, before line 1, please insert the following before the first paragraph:

DETAILED DESCRIPTION OF THE INVENTION

IN THE CLAIMS:

Please cancel claims 9 and 10 without prejudice.

Please amend claims 3-8 as follows:

3. (Amended) A process according to any one of the preceding claims claim 1, wherein the catalyst is present in an amount ranging from about 5 ppb to about 5000 ppb, preferably from 100 ppb to about 1000 ppb, on dry substance of starch.

4. (Amended) A process according to ~~any one of the preceding claims~~ claim 1, wherein the action of the divalent copper ions is enhanced by one or more of calcium, vanadium, manganese, iron or tungsten ions.

5. (Amended) A process according to ~~any one of the preceding claims~~ claim 1, wherein the starch is a potato starch or tapioca starch.

6. (Amended) A process according to ~~any one of the preceding claims~~ claim 1, wherein the hydrogen peroxide is used in an amount ranging from 0.01 to 5.0 wt%, preferably from 0.05 to 2.5 wt% on dry substance of starch.

7. (Amended) A process according to ~~any one of the preceding claims~~ claim 1, wherein the derivative of the starch is a cationic, anionic or amphoteric starch.

8. (Amended) An oxidized starch obtainable by a process according to ~~any one of the preceding claims~~ claim 1.

Please add new claims 11-18, as follows:

11. A binder in paper coatings or surface coatings comprising an oxidized starch according to claim 1.

12. An adhesive comprising an oxidized starch according to claim 1.

13. A warp yarn sizing comprising an oxidized starch according to claim 1.

14. A coating for glass fibers comprising an oxidized starch according to claim 1.

15. An abrasive paper additive comprising an oxidized starch according to claim

16. A food product additive comprising an oxidized starch according to claim 1.

17. A blanket adhesive comprising an oxidized starch according to claim 1.

18. An emulsifying agent for an alkyl succinic anhydride, alkyl ketene dimer or alkyl isocyanate comprising an oxidized starch according to claim 1.

AFTER THE CLAIMS

Please insert, after the claims, on a separate sheet:

ABSTRACT

The invention relates a process of oxidizing starch wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions. The present invention further relates to an oxidizable starch obtainable by a process comprising treating a starch with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

Title: Oxidation of starch

The invention relates to the oxidation of starch.

The oxidation of starch is usually carried out in order to reduce the viscosity of the starch in solution or dispersion. During the oxidation reaction, starch molecules 5 are broken down, yielding molecules having a decreased molecular weight.

Oxidized starches have found many applications in industry. Examples of common applications include the use of oxidized starch in the paper industry, for instance in 10 coatings or surface sizing, the adhesive industry, the textile industry, and the food industry.

The preparation of oxidized starches is conventionally carried out by oxidation with an alkali metal hypochlorite, which is a relatively cheap oxidizing agent.

15 The oxidation of starch using an alkali metal hypochlorite is extensively described in the literature (see among others "Modified Starches: Properties and Uses", O.B. Wurzburg, CRC Press Inc., 1987).

20 Although the oxidation of starch using an alkali metal hypochlorite is an efficient reaction, leading to high yields of desired product in a relatively short reaction time, it has some disadvantages. One disadvantage is that a large amount of salts is produced, in particular chloride salts, during the oxidation. Other disadvantages are the risk 25 of chlorine formation during the reaction and of the occurrence of unacceptably high AOX levels.

In order to overcome the problems associated with these disadvantages, attempts have been made to find an alternative oxidizing agent. One alternative oxidizing agent 30 that has received a significant amount of attention is hydrogen peroxide.

As early as in 1933, in the German Patent 738909, a process has been described wherein starch is oxidized using only hydrogen peroxide as oxidizing agent. The reaction is 35 performed under semi-dry conditions at a temperature below

60°C. The obtained oxidized starch product was intended to be used in puddings. It has meanwhile been found, however, that this process does not lead to a considerable extent of break down of the starch molecules in a reasonable reaction time.

5 In other words, the disclosed process is very slow.

In order to improve the reaction rate of the oxidation of starch using hydrogen peroxide, it has been proposed to use metal catalysts in said oxidation reactions. In the international patent application WO-A-97/35888, it has 10 been proposed to use metal based coordination complexes as catalysts in an alkaline slurry reaction of starch with hydrogen peroxide. The disclosed coordination complexes are based on a transition metal selected from groups VIIb, VIIb,, VIIIb or the lanthanide series of the Periodic Table. The 15 complexes further comprise an organic ligand containing at least three nitrogen atoms which coordinate to the metal, and a bridging group.

From US patent 3,655,644, the use of copper as a catalyst in the oxidation of starch using hydrogen peroxide is known. Although the patent mentions general amounts of 20 copper of from 5 to 100 ppm, according to the examples at least 50 ppm needs to be used.

Disadvantages of the known processes for oxidizing starch using hydrogen peroxide and a metal based catalyst are 25 that undesirably high amounts of catalyst (50 ppm) are required in order to be able to degrade the starch to a sufficient extent (intrinsic viscosity 0,1 - 1,5 dL/g) within a reasonable reaction time (less than 24 hours).

The present invention aims to provide a process for 30 oxidizing starch using hydrogen peroxide, which process does not have the disadvantages of the prior art. More in particular, it is an object of the invention to provide a process for oxidizing starch using hydrogen peroxide, which process leads to a sufficiently degraded starch product in a 35 relatively short reaction time.

Surprisingly, it has been found that the above objectives may be reached by starting from a specific type of starch, which has a very low amylose content. Thus, the invention relates to a process of oxidizing starch, wherein a 5 root or tuber starch comprising at least 95 wt.% based on dry substance of the starch of amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

In a process according to the invention, very small 10 amounts of the catalyst suffice in order to provide a process having a high reaction rate. The process of the invention leads, in a short time, to an oxidized starch having a desirably low viscosity and high stability, when in solution.

As has been indicated above, according to the 15 invention, a root or tuber starch is oxidized, which starch has a very high amylopectin content. Most starch types consist of granules in which two types of glucose polymers are present. These are amylose (15-35 wt.% on dry substance) and amylopectin (65-85 wt.% on dry substance). Amylose 20 consists of unbranched or slightly branched molecules having an average degree of polymerization of 1000 to 5000, depending on the starch type. Amylopectin consists of very large, highly branched molecules having an average degree of polymerization of 1,000,000 or more. The commercially most 25 important starch types (maize starch, potato starch, wheat starch and tapioca starch) contain 15 to 30 wt.% amylose.

Of some cereal types, such as barley, maize, millet, wheat, milo, rice and sorghum, there are varieties of which the starch granules nearly completely consist of amylopectin. 30 Calculated as weight percent on dry substance, these starch granules contain more than 95%, and usually more than 98% amylopectin. The amylose content of these cereal starch granules is thus less than 5%, and usually less than 2%. The above cereal varieties are also referred to as waxy cereal 35 grains, and the amylopectin starch granules isolated therefrom as waxy cereal starches.

In contrast to the situation of different cereals, root and tuber varieties of which the starch granules nearly exclusively consist of amylopectin are not known in nature. For instance, potato starch granules isolated from potato tubers usually contain about 20% amylose and 80% amylopectin (wt.% on dry substance). During the past 10 years, however, successful efforts have been made to cultivate by genetic modification potato plants which, in the potato tubers, form starch granules consisting for more than 95 wt.% (on dry substance) of amylopectin. It has even been found feasible to produce potato tubers comprising substantially only amylopectin.

In the formation of starch granules, different enzymes are catalytically active. Of these enzymes, the granule-bound starch synthase (GBSS) is involved in the formation of amylose. The presence of the GBSS enzyme depends on the activity of genes encoding for said GBSS enzyme. Elimination or inhibition of the expression of these specific genes results in the production of the GBSS enzyme being prevented or limited. The elimination of these genes can be realized by genetic modification of potato plant material or by recessive mutation. An example thereof is the amylose-free mutant of the potato (amf) of which the starch substantially only contains amylopectin through a recessive mutation in the GBSS gene. This mutation technique is described in, inter alia, J.H.M. Hovenkamp-Hermelink et al., "Isolation of amylose-free starch mutant of the potato (*Solanum tuberosum L.*)", *Theor. Appl. Gent.*, (1987), 75:217-221, and E. Jacobsen et al., "Introduction of an amylose-free (amf) mutant into breeding of cultivated potato, *Solanum tuberosum L.*", *Euphytica*, (1991), 53:247-253.

Elimination or inhibition of the expression of the GBSS gene in the potato is also possible by using so-called antisense inhibition. This genetic modification of the potato is described in R.G.F. Visser et al., "Inhibition of the expression of the gene for granule-bound starch synthase in

potato by antisense constructs", Mol. Gen. Genet., (1991), 225:289-296.

By using genetic modification, it has been found possible to cultivate and breed roots and tubers, for 5 instance potato, yam, or cassave (Patent South Africa 97/4383), of which the starch granules contain little or no amylose. As referred to herein, amylopectin potato starch is the potato starch granules isolated from potato tubers and having an amylopectin content of at least 95 wt.% based on 10 dry substance.

Regarding production possibilities and properties, there are significant differences between amylopectin potato starch on the one hand, and the waxy cereal starches on the other hand. This particularly applies to waxy maize starch, 15 which is commercially by far the most important waxy cereal starch. The cultivation of waxy maize, suitable for the production of waxy maize starch is not commercially feasible in countries having a cold or temperate climate, such as The Netherlands, Belgium, England, Germany, Poland, Sweden and 20 Denmark. The climate in these countries, however, is suitable for the cultivation of potatoes. Tapioca starch, obtained from cassave, may be produced in countries having a warm climate, such as is found in regions of South East Asia and South America.

25 The composition and properties of root and tuber starch, such as amylopectin potato starch and amylopectin tapioca starch, differ from those of the waxy cereal starches. Amylopectin potato starch has a much lower content of lipids and proteins than the waxy cereal starches. 30 Problems regarding odor and foaming, which, because of the lipids and/or proteins, may occur when using waxy cereal starch products (native and modified), do not occur, or occur to a much lesser degree when using corresponding amylopectin potato starch products. In contrast to the waxy cereal 35 starches, amylopectin potato starch contains chemically bound phosphate groups. As a result, amylopectin potato starch

products in a dissolved state have a distinct polyelectrolyte character.

According to the invention, root and tuber starches are oxidized. Surprisingly, under the conditions of the present process, cereal and fruit starches are not degraded to a sufficient extent to obtain a product having the desired characteristics. The oxidation of amylopectin potato starch and amylopectin tapioca starch has been found to lead to particularly advantageous oxidized starches.

Suitable derivatives of the above specific starch to be used in an oxidation process according to the invention are obtainable by crosslinking, etherification, or esterification of the starch, or a combination of two or more of said modifications. These modifications may be performed in any known manner. Examples of suitable manners for obtaining the desired derivatives are for instance disclosed in "Modified Starches: Properties and Uses", O.B. Wurzburg, CRC Press Inc., 1987.

Within these classes of derivatives, particularly preferred derivatives to be oxidized are cationic, anionic and amphoteric starches. For the introduction of a cationic group, preferably a 2-hydroxypropyltrialkyl ammonium group is introduced on the starch. The alkyl chains of this quaternary ammonium compound may vary from 1 to 20 carbon atoms. For example, 1-chloro-2-hydroxypropyltrimethyl ammonium salt, glycidyltrimethyl ammonium salt, 1-chloro-2-hydroxypropyldimethylallyl ammonium salt or 1-chloro-2-hydroxypropylmethyldiallyl ammonium salt can be applied as cationization agent. Anionic substituents can be attached to the starch via an ether linkage. This may be achieved by reaction with for example chloroacetic acid or chloroacetic acid salts. Amphoteric derivatives may comprise any combination of the above cationic and anionic groups.

According to the invention, starch is oxidized using hydrogen peroxide. The amount of hydrogen peroxide employed is from about 0.01 to 5.0 wt.%, preferably about 0.05 to 2.5

wt.% anhydrous hydrogen peroxide on dry substance of the starch. The hydrogen peroxide will normally be used in the form of an aqueous solution, as commonly supplied in commerce.

5 Preferably, the oxidation reaction is performed in a solution, dispersion or suspension of the starch in water, to which the hydrogen peroxide, or an aqueous solution thereof, is added. Preferably, the hydrogen peroxide is added batchwise or dropwise.

10 Suitable concentrations of the starch in said solution, dispersion or suspension lie between 10 and 50, preferably between 20 and 40 wt.%, based on the weight of the solution, dispersion or suspension. The pH during the oxidation reaction will preferably around neutral and lie 15 between pH 6.5 and 9.0. The temperature during the oxidation reaction in a suspension will preferably be below 60°C, more preferably between 20 and 50°C. When the reaction is carried out in a solution or dispersion, the temperature will usually be chosen between 60 and 200°C, preferably between 100 and 20 160°C. In order to carry out the reaction at a temperature higher than 100°C, use is preferably made of a jet cooker.

25 In accordance with the present invention, the oxidation of the specific starch described above is performed in the presence of a catalyst, which catalyst comprises 30 divalent copper ions. The catalyst will preferably be used in the form of a salt. In principle, any copper(II)-salt which is soluble in water may be used. Suitably, the anion of the salt may be chosen from the group of chloride, sulfate, phosphate, nitrate, acetate, bromide and combinations thereof.

35 It is one of the great advantages of the present invention that the oxidation reaction proceeds very fast to a desired extent of degradation of the starch, while only very small amounts of the catalyst are used. More in particular, it has been found that such small amounts of catalyst suffice, that the amount of metal ions that ends up in the

process water (mother liquor) is acceptably low. Said process water can conveniently be disposed together with normal sludge disposal without encountering the risk that the microorganisms present in the sludge are exterminated.

5 Preferably, the quantity of copper used ranges from about 5 ppb to about 5000 ppb, more preferably from about 100 to about 1000 ppb, on dry substance of starch. When the oxidation reaction is carried out in a solution or a dispersion, the quantity of copper may be lower (e.g. between 10 5 and 1000 ppb) than when the reaction is performed in a suspension.

In a preferred embodiment, the action of the divalent copper ions is enhanced by calcium, vanadium, manganese, iron and/or tungsten ions. The counterions for these ions may be 15 of the same type as those of the copper catalyst. These additional salts will preferably be used in an amount between about 100 and about 2000 ppm, on dry substance of starch.

The invention further relates to an oxidized starch obtainable by a process as described hereinabove, and to the 20 use of said oxidized starch in the paper, adhesive, textile and food industries.

In the paper industry, oxidized starches have been used as coating binders since 1903. The main purpose of coating paper is to improve its printability. The most 25 important components of a coating (also referred to as coating color) are pigments, such as titanium oxide, calcium carbonate, clays, and the like, binders, such as latices, starches, PVOH, proteins, and the like, and water. The present oxidized starches have been found to have excellent 30 properties, such as a good viscosity stability when in solution or dispersion. This makes them highly suitable for use as a binder in paper coatings.

In another application, the present oxidized starch, particularly when prepared from a cationic starch derivative, 35 may be used as an emulsifying agent for, or during production of, alkyl ketene dimers, alkyl succinic anhydride or alkyl

isocyanates (analogous to what has been described in e.g. WO-A-96/31650, EP-A-0 824 161 and EP-A-0 369 328).

In addition, it has been found that the present oxidized starch is highly suitable for replacing high viscous 5 hydrocolloids, such as polyvinyl alcohol, guar, alginate, carboxymethylcellulose or hydroxyethylcellulose.

Yet another application wherein the present oxidized starch has been found to be highly suitable is in adhesives. The present oxidized starch may be used to adhere two or more 10 layers of paper together to form a multi-layer paper or (card)board. Also, aluminum foil can suitably be adhered onto paper by use of an oxidized starch according to the invention. Further, the present oxidized starch may be used as a component in paper sack adhesives and wall paper 15 adhesives, leading to an adhesive providing improved binding strength. In addition, paper and tape may be gummed with the present oxidized starch to produce stamps or envelopes. In abrasive paper or abrasive linen, the present oxidized starch may be used to adhere abrasive particles, such as sand, onto 20 the paper or linen. In addition, the present oxidized starch may be used as an adhesive for seeds or fertilizers.

Still another application is related to the stabilization of emulsions, in particular of emulsions used in the adhesive industry such as polyvinylacetate emulsions. 25 An oxidized starch according to the invention may be used as a protective colloid for providing the desired stability.

In the textile industry, the present oxidized starch may be used to improve the weaving operation or weaving efficiency by warp yarn sizing. This results in an improved 30 abrasion resistance of the warp yarns during the weaving process and less warp-end breakages. The present oxidized starch may further be applied as finishing agent to give a smooth and firm hand to fabrics. It may also be used for the coating of glass fibers (fabrics and non-wovens). In 35 addition, it may be used as blanket adhesive in the textile printing industry.

In the food industry, Arabic gum may be replaced in e.g. confectioneries by an oxidized starch according to the invention. Also, the present product has been found to be highly suitable as a thickener in various food products, such 5 as sauces. The excellent stability of the present oxidized starch, leads in these applications to a more clear food product.

It will be clear to the skilled person that the above list of applications is not intended to be extensive and that 10 many more applications of the present oxidized starches are conceivable. In practice, the present product may be used in any application in which oxidized starches have conventionally been used.

15 The invention will now be elucidated by the following non-restrictive examples.

EXAMPLES

20 Brookfield viscosity

The Brookfield viscosity (in mPa.s.) is measured at a 25 w/w% solution (dispersion) of the product in water at 50°C with a Brookfield viscometer (model RV-II+; 20 rpm). The stability of the starch solution was determined by measuring the 25 Brookfield viscosity after 24 hours of storage at 50°C.

Intrinsic viscosity

The intrinsic viscosity, expressed in dL/g, is determined in a known manner, for instance as described in H.W. Leach in 30 Cereal Chemistry, vol. 40, page 595 (1963), using an Ubbelohde viscosity meter and a 1 M sodium hydroxide in water as the solvent.

Peroxide test

35 The peroxide test is performed with Merckoguant 1.10081.0001 peroxide-test analytical test strips. The test was positive,

indicating that there was still some hydrogen peroxid in the reaction mixture, or negative, indicating that the hydrogen peroxide was consumed.

5 Example 1

2.5 mole of amylopectin potato starch was suspended in 633 g of demineralized water. The temperature of the suspension was increased to 40°C and 2.7 mL of a solution of 550 mg CuSO₄.5H₂O in 1 L of demineralized water was added. 20 ml of 10 a 30 wt.% hydrogen peroxide solution in water was added. During the oxidation the pH was maintained at 7.0 by the addition of a 4.4% sodium hydroxide solution in demineralized water. After 24 h of the reaction mixture the peroxide test was carried out. Subsequently, the mixture was neutralised to 15 pH 5.0 by the addition of 10 N H₂SO₄, whereupon the product was dewatered and washed before drying.

Instead of amylopectin potato starch, potato starch, waxy corn starch or tapioca starch was used as starting material. 20 Besides, 5.4 mL of a solution of 550 mg CuSO₄.5H₂O in 1 L of demineralized water was added in stead of 2.7 mL. The results are shown in table 1.

Table 1 - The hydrogen peroxide oxidation of different starches at (8.0 g hydrogen peroxide per mole starch, 40°C, pH 7.0, during 24 hour) catalyzed by various amounts of copper-ions.

5

| Starch-type (intrinsic viscosity starting material) | Cu ppb ³ | Peroxide test | Intrinsic viscosity (dL/g) | Brookfield viscosity (mPa.s.) after 0 and 24 hours storage at 50°C | |
|-----------------------------------------------------------------|------------------------|------------------|----------------------------------|-----------------------------------------------------------------------------|------|
| | | | | 0 h | 24 h |
| Potato | 0 | positive | 2.54 ² | n.a. ¹ | |
| | 932 | positive | 2.52 | 100.000 | gel |
| | 1858 | negative | 0.28 | 50.000 | gel |
| Waxy-corn | 932 | positive | 1.69 ² | n.a. ¹ | |
| | 1858 | positive | 1.66 | n.a. ¹ | |
| Tapioca | 932 | positive | 1.50 | | |
| | 1858 | positive | 2.19 ² | n.a. ¹ | |
| Amylopectin potato | 0 | positive | 1.17 | n.a. ¹ | |
| | 932 | positive | 0.75 | n.a. ¹ | |
| | 1858 | negative | 2.26 ² | n.a. ¹ | |
| | 0 | positive | 1.85 | 37 | 37 |
| | 932 | negative | 0.20 | | |
| | 1858 | negative | 0.20 | 35 | 37 |

¹ n.a. = not available due to very high viscosity of the 25 w/w % suspension of the product

² Intrinsic viscosity of the starting material

10 ³ Amount of catalyst calculated on dry starch

Comparison of the results presented in table 1, shows that the hydrogen peroxide degradation of starch catalyzed by small amounts of copper ions is more efficient in the order:

15 waxy corn starch < tapioca starch < potato starch <

amylopectin potato starch. Without the addition of copper ions the hydrogen peroxide of potato starch is negligible. Under the same reaction conditions amylopectin potato starch reacts slowly.

5 Besides, it can be seen that the viscosity of the solution of the degraded amylopectin potato starch during storage at 50°C is very stable. A solution of the degraded potato starch is very unstable and a gel is formed.

10 Example 2

The reaction of Example 1 was repeated with amylopectin potato starch and 0.0125 mole of calcium ions instead of CuSO₄.5H₂O.

The results are presented in table 2.

15

Example 3

The reaction of Example 1 was repeated with amylopectin potato starch and 0.0125 mole of calcium ions and 0.36 mL of a solution of 550 mg CuSO₄.5H₂O in 1 L of demineralized water 20 instead of 2.7 mL of a solution of 550 mg CuSO₄.5H₂O in 1 L of demineralized water.

The results are presented in table 2.

25 Table 2 - The hydrogen peroxide oxidation of amylopectin potato starch at (8.0 g hydrogen peroxide per mole starch, 40°C, pH 7.0, during 24 hours) catalyzed by 1240 ppm calcium ions and a combination of 1240 ppm calcium ions and 110 ppb copper-ions.

| Cu ppb ¹ | Peroxid test | Brookfield viscosity (mPa.s.) | Intrinsic viscosity (dL/g) |
|------------------------|-----------------|-------------------------------------|----------------------------------|
| 0 | positive | 5150 | 1.38 |
| 110 | positive | 1620 | 1.10 |

30

¹ Amount of catalyst calculated on dry starch

The hydrogen peroxide oxidation of amylopectin potato starch is catalyzed by calcium ions. Calcium ions are less effective than copper ions. The combination of calcium ions and copper ions lead to a more effective degradation of the amylopectin potato starch.

Example 4

2.5 mole of cationic (MSin = 0.035) amylopectin potato starch was suspended in 633 g of demineralized water. The temperature of the suspension was increased to 40°C and 2.7 mL of a solution of 550 mg CuSO₄.5H₂O in 1 L of demineralized water was added. 1.25 ml of a 30 wt.% hydrogen peroxide solution in water was added. During the oxidation the pH was maintained at 7.0 by the addition of a 4.4% sodium hydroxide solution in demineralized water. After 24 h of the reaction mixture the peroxide test was carried out. Subsequently, the mixture was neutralised to pH 5.0 by the addition of 10 N H₂SO₄, whereupon the product was dewatered and washed before drying.

Instead of cationic amylopectin potato starch, cationic potato starch (MSin = 0.035) was used as starting material. Besides, 2.5, 5.0 or 7.5 mL of a 30 wt.% hydrogen peroxide solution in water was added instead of 1.25 mL. The results are summarized in Table 3.

Table 3 - The hydrogen peroxide concentration of cationic potato starches (932 ppb Cu²⁺, 40°C, pH 7,0 during 24 hours)

5

| Starch type | 30 wt.% H ₂ O ₂ (mL/mol) | Peroxide test | Brookfield viscosity (mPa.s.) in 10 wt.% concentration |
|------------------------------------|------------------------------------------------|---------------|--------------------------------------------------------|
| Cationic potato starch | 0,50 | positive | 2300 |
| | 1,00 | positive | 290 |
| | 2,00 | positive | 66 |
| | 3,00 | positive | 28 |
| Cationic amylopectin potato starch | 0,50 | negative | 250 |
| | 1,00 | negative | 83 |
| | 2,00 | negative | 33 |
| | 3,00 | negative | 18 |

Example 5

2000 Grams of starch were suspended in 2L of water. To this suspension, 120 grams of a 25% solution of NaOH was added.

The suspension was stirred for 30 minutes at 90°C.

Subsequently, 75 grams of a 30% aqueous solution of hydrogen peroxide was added and the stirring was continued at the same temperature. The conditions employed are illustrative of a thermochemical conversion process.

The above procedure was performed twice. Once, the starch was regular potato starch (PS), and once the starch was amylopectin potato starch (APS). In the case of APS, the reaction was complete after 30 minutes, which was determined by establishing that no hydrogen peroxide was present. The obtained product was stable. In the case of PS, the reaction was complete after 60 minutes, which was determined by establishing that no hydrogen peroxide was present. The

obtained product was very unstable; even at 90°C a thickening effect was observed.

Claims

1. A process of oxidizing starch wherein a root or tuber starch comprising at least 95 wt.% based on dry substance of the starch of amylopectin, or a derivative thereof, is treated with hydrogen peroxide in the presence of a catalyst, which catalyst comprises divalent copper ions.

2. A process according to claim 1, wherein the catalyst is a copper(II)chloride, copper(II)sulfate, copper(II)phosphate, copper(II)nitrate salt, copper(II)acetate salt, copper(II)bromide salt or a combination thereof.

3. A process according to any one of the preceding claims, wherein the catalyst is present in an amount ranging from about 5 ppb to about 5000 ppb, preferably from 100 to about 1000 ppb, on dry substance of starch.

4. A process according to any one of the preceding claims, wherein the action of the divalent copper ions is enhanced by one or more of calcium, vanadium, manganese, iron or tungsten ions.

5. A process according to any of the preceding claims, wherein the starch is potato starch or tapioca starch.

6. A process according to any one of the preceding claims, wherein the hydrogen peroxide is used in an amount ranging from 0.01 to 5.0 wt.%, preferably from 0.05 to 2.5 wt.% on dry substance of starch.

7. A process according to any one of the preceding claims, wherein the derivative of the starch is a cationic, anionic or amphoteric starch.

8. An oxidized starch obtainable by a process according to any one of the preceding claims.

9. Use of an oxidized starch according to claim 8 as a binder in paper coatings or surface sizings, as an adhesive, in warp yarn sizing, as a coating of glass fibers, as a blanket adhesive, and in abrasive paper or in food products.

10. Use of an oxidized starch according to claim 8 as an emulsifying agent for an alkyl succinic anhydride, an alkyl ketene dimer or an alkyl isocyanate.



Declaration and Power of Attorney Patent Application (Design or Utility)

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name,

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: 'Oxidation of starch'

the specification of which

is attached hereto
 was filed on February 21, 2001 as application serial no.
and or PCT International Application number PCT/NL99/00568 and was amended
on (if applicable).

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §119(a)-(d) or 35 U.S.C. §365(b) of any foreign application(s) for patent or inventor's certificate, or 35 U.S.C. §365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below any foreign application for patent or inventor's certificate of PCT International application having a filing date before that of the application on which priority is claimed.

| Prior Foreign Application(s) | | |
|------------------------------|---------|----------------------|
| Number | Country | Day/Month/Year Filed |
| 98203043.9 | EP | 11-09-1998 |
| Number | Country | Day/Month/Year Filed |
| Number | Country | Day/Month/Year Filed |

I hereby claim the benefit under 35 U.S.C. §119(e) of any United States provisional application(s) listed below:

| Prior Provisional Application(s) | |
|-----------------------------------------|-----------------------------------|
| Serial Number | Day/Month/Year Filing Date |
| Serial Number | Day/Month/Year Filing Date |
| Serial Number | Day/Month/Year Filing Date |

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s), or under 35 U.S.C. §365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose to the U.S. Patent and Trademark Office all information known to me to be material to patentability as defined in 37 C.F.R. §1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application:

| Prior U.S. or International Application(s) | | |
|---------------------------------------------------|-----------------------------|----------------------------------------------|
| Serial Number | Day/Month/Year Filed | Status (patented, pending, abandoned) |
| Serial Number | Day/Month/Year Filed | Status (patented, pending, abandoned) |
| Serial Number | Day/Month/Year Filed | Status (patented, pending, abandoned) |

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements are made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.



Power of Attorney

As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby authorize them or others whom they may appoint to act and rely on instructions from and communicate directly with the person/organization who/which first sends this case to them and by whom/which I hereby declare that I have consented after full disclosure to be represented unless/until I instructed otherwise.

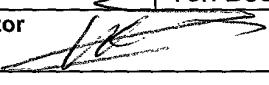
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